

Reply to anonymous Referee #1

We thank anonymous Referee #1 for the thoughtful review. Especially the comments on turnover rates will help to improve the manuscript (see below). Detailed responses to the different issues raised in the review can be found below. To facilitate the revision, the comments from Referee #1 are written in blue whereas our responses are in black.

Anonymous Referee #1: As mentioned above, I think I would put the emphasis a little different. The authors very delicately suggest the option of overprint of the signal by advection of allochthonous alkenones especially at low alkenone concentrations. I think this is most likely the main reason for the lack of temperature and δD correlations between measured and alkenone derived values when the low concentration samples are included. Alkenones are less susceptible to degradation resulting in a relatively large fraction old or “fossil” alkenones in every individual SPM sample and this fraction is probably larger at low concentrations. The turnover rate of fatty acids is higher than that of alkenones and a large fraction of the C16 FAs will have been produced in the water mass they were obtained from, resulting in a better correlation between the C16 FA δD and water mass properties.

Response: We agree that alkenones are less susceptible to degradation than palmitic acid and that the δD values recorded in palmitic acid are therefore less susceptible to overprint by pre-formed compounds. Accordingly, we expanded section 4.3.2. *Palmitic acid δD* of the manuscript to that regard. Our hesitation to give this line of argument more room in our discussion mainly stems from the observation that temperature reconstructions based on alkenones also show large deviations. Unlike salinity values in the Amazon continental margin that are subject to fast and large changes, temperature values are fairly stable and there is no nearby water mass that would provide fossil alkenones with a temperature signal as low as the one reconstructed (see page 10, lines 8-12 of the original version of the manuscript). In our opinion, lower haptophyte growth rates due to light limitation and low salinity are an elegant way to explain this bias, since they potentially account for both the δD and temperature deviations.

Anonymous Referee #1: SPM samples represent a snapshot in time and space which makes it really easy to miss an algal bloom or the production season of specific biomarker lipids such as alkenones. In that sense it would have been nice to compare the presented results with cell counts or molecular technique based community composition estimates. There are for instance alkenone producing haptophytes that thrive in low salinity environments, but their production season might be different from the more open ocean species (assuming that the authors did catch the open ocean alkenone production season). The “fossil” alkenones that affect the UK and δD correlations at low concentrations might be derived from other water masses, but also from different time intervals, possibly re-suspended from the (shelf) sediment and transported by the Amazon outflow. This is exactly why the authors suggest to analyze both C16 FAs (or another more general lipid) and alkenones and I think that is a good suggestion.

Response: Having sampled the study area during one single cruise (Mulitza et al., 2013) we might indeed have missed the main algal bloom season of certain alkenone producing species. We also agree that cell counts and/or other molecular techniques would have been a nice addition to our study. However, this was beyond the scope of the study and we relied on the C_{37}/C_{38} ratio to assess different haptophyte sources (e.g. Conte et al., 1998). Our results based on the C_{37}/C_{38} ratio do not suggest a

large scale shift to coastal alkenone producers (see page 4, lines 4-17 of the original version of the manuscript).

Anonymous Referee #1: However, the C16 FA has its own potential biases. It has become clear that the hydrogen isotopic composition of lipids from photoautotrophic organisms are correlated with salinity and/or reflect the δD of the water and photoautotrophic organisms fractionate to a similar extent. However, heterotrophic organisms fractionate very differently and might show no or a different relationship with salinity. The C16 FA can be derived from many different organisms and different contributions from organisms with different metabolisms could potentially affect the hydrogen isotopic composition of FAs. Fortunately, it seems that in many of these open ocean water column ecosystems photoautotrophic microorganisms are the dominant contributors to the C16 FA pool. The high turnover rate of the fatty acids also make them less interesting for paleo reconstructions on longer time scales.

Response: We agree that heterotrophic organisms could lead to changes in palmitic acid δD in sedimentary records (see page 14, lines 21-23 of the original version of the manuscript). The question is whether the heterotrophic contribution in the water column and in the sediment is large enough to significantly overprint the original phototrophic signal. There are some reassuring studies showing that the influence of heterotrophic organisms is not large enough to alter the signal of phototrophic organisms (Huang et al. 2004, Li et al. 2009) which also seems to be the case in the Amazon Plume. Besides the potential influence by heterotrophs, there are also variations in palmitic acid isotopic fractionation factor for different species of phototrophic organisms (e.g. haptophyte algae) (Chivall et al. 2014). In our study, these variations appear to have no influence on the isotopic fractionation on an ecosystem level. To rule out these effects, we propose to test the consistency of a down core δD signal among multiple lipids (see page 14, lines 24-25 of the original version of the manuscript).

Anonymous Referee #1: I think the authors should emphasize the difference in turnover rates between FAs and alkenones a bit more and the perhaps put less emphasis on less alkenone production at low salinities.

Response: We agree that turnover rates between alkenones and palmitic acids are different and expanded on the role of turnover rates in section 4.3.2. *Palmitic acid δD* of the manuscript. We do, however, maintain that turnover rates alone are insufficient to explain the observed patterns. Lower turnover rates alone would not explain the salinity relationship of alkenone concentration that is clearly visible in our data (see Figure 2c of the original version of the manuscript) and is also insufficient to explain the large temperature deviation in our data (see Figures 2b and 4b of the original version of the manuscript).

Page 2; line 14 to 19: I don't think it is necessarily true that alkenone production is low at low salinity, light limitation is something different. With sampling SPM during a cruise it is relatively easy to miss the main "production" season. Haptophyte community composition analysis might help answer these questions in the future.

Response: In the studied area, light limitation and low salinity are coinciding, since Amazon derived freshwater is extremely suspension rich (Smith and Demaster 1996). Hence, the two effects work in concert and are generally hard to disentangle. The abstract of the manuscript was amended to clarify

this issue. In terms of haptophyte composition analysis, we fully agree that community analysis would have been interesting, but was unfortunately beyond the scope of this study.

Page 4; line 1 to 3: This is not what Kasper et al. 2015 have suggested. They suggested that there is no clear glacial interglacial δD alkenone shift because during the glacial the core location was closer to the coast due to low sea level, resulting in more freshwater influence (low salinity and δD water) and more negative δD alkenone values than “normally” found during glacials. On top of that there might be a small species effect. Species variability did not make salinity reconstructions impossible, they suggest that salinity might not have changed that much.

Response: Page 4, lines 1-3 were corrected. The sentence now reads: “However, in some cases, factors like species variability complicated δD based salinity reconstructions.”

Page 10; line 19: Schouten et al., 2006 does not discuss coastal haptophytes. This reference belongs to the first half of this sentence.

Response: The Schouten et al. (2006) reference was moved to the first half of the sentence.

Page 12; line 17 to 19: I agree that at low alkenone concentrations the fraction “fossil” might be large and affecting α , for instance, but could it be possible the authors missed the haptophyte bloom and/or main alkenone production season?

Response: It is possible that we missed the main haptophyte bloom, which would have made advection more likely. As outlined above, we do not think that advection is the dominant factor responsible for the deviations in δD .

References

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